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## EUROPEAN PATENT APPLICATION

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㉓ Bis(benzotriazoly)benzophenones and their use as UV absorbers.

㉔ The invention relates to UV absorbers which are benzotriazoly hydroxy benzophenones and which may be incorporated into plastics materials or polymerised with other monomers such as acrylates or methacrylates. The formed polymers or polymer composition may be employed for the manufacture of articles such as intraocular lens, contact lens and eyeglasses.

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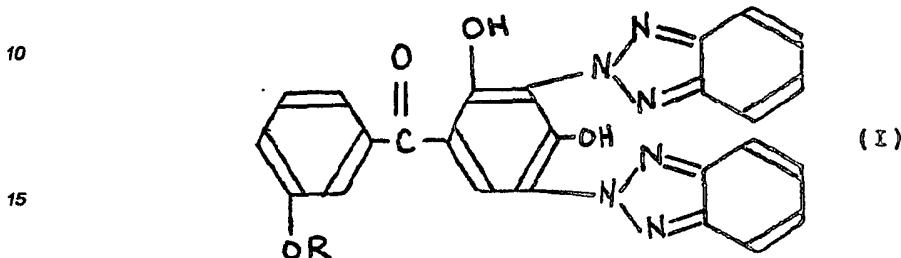
Jouve, 18, rue Saint-Denis, 75001 PARIS

## UV ABSORBERS &amp; PRODUCTS CONTAINING SAME

This invention relates to UV absorbers, to polymer compositions containing such absorbers and to articles made from such UV absorber-containing polymer compositions. More particularly the invention relates to a novel ultraviolet absorber, to acrylic polymers having incorporated therein a UV absorbing amount of the UV absorber, to intraocular lenses and contact lenses formed from said acrylic polymers and to eyeglasses formed from a polycarbonate material which contains a UV absorbing amount of the UV absorber.

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In accordance with the present invention there is provided a compound of the formula (I)



wherein R is hydrogen or  $\text{CO.CR}' = \text{CH}_2$ , wherein R' is hydrogen or methyl.

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Preferred compounds of Formula (I) are :

3,5[Bis(2H-benzotriazol-2-yl)] 2,4,4'-trihydroxybenzophenol (BTHB) and  
3,5[Bis(2H-benzotriazol-2-yl)]2,4-dihydroxy 4'-acryloyloxybenzophenone (BTAB).

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The compounds of the present invention may be produced by conventional techniques. For example, the triazole component may be first produced by conventional diazotising techniques followed by reaction with the appropriate benzophenone. The resultant ditriazole can then be esterified, for example, by acylation with an appropriate acrylic component to produce a polymerisable triazole.

These compounds are effective for absorbing UV light in the range of about 200 nm to about 450 nm particularly in the range of 240 nm to 420 nm.

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The present invention also provides a polymer composition comprising a UV absorbing amount of the compound of Formula I herein.

The polymer composition may be a polymer per se comprising residues derived from a acrylically unsaturated monomer eg. methyl methacrylate and a UV absorbing amount of residues derived from the compound of Formula I herein.

The UV absorber-containing acrylic polymers of the present invention are believed to have the formula (II)

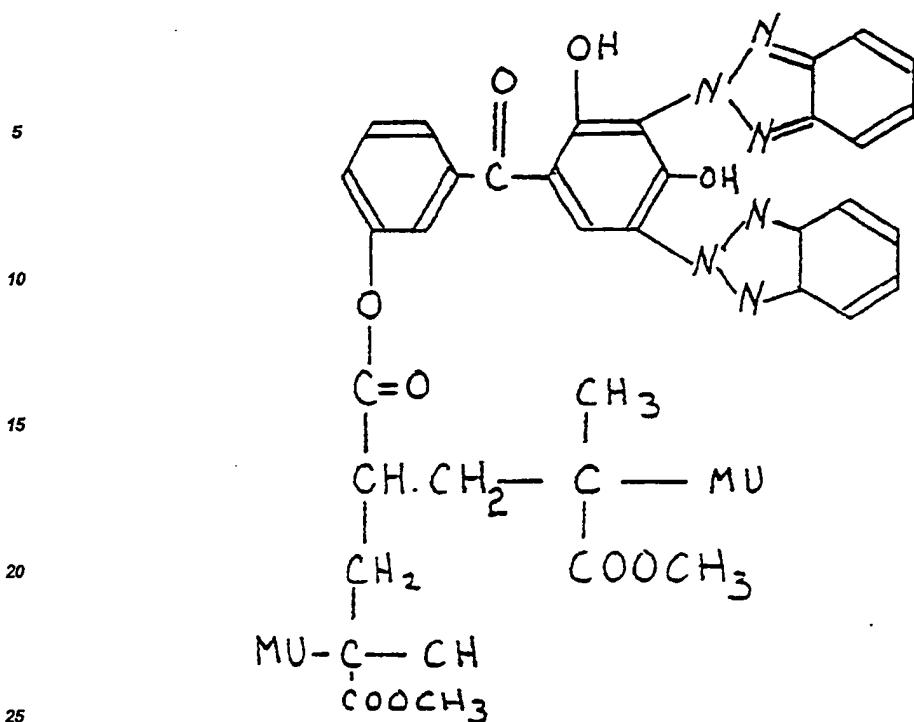
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wherein MU is the monomer unit.

Preferred polymers are those derived from methylmethacrylate. Other polymers may comprises residues derived from other acrylically unsaturated compounds such as acrylates or methacrylates for example hydroxyethylmethacrylate.

The amount of compound of formula I required to be a effective UV absorber will generally be greater than 0.1% by weight of the total composition. Normally the amount of UV absorber need not exceed 5% by weight of the composition. Thus the UV absorber of Formula I may aptly be included in the polymer or polymer composition in an amount of from 0.1% to 5% by weight based on the weight of the polymer composition. Suitably 35 0.1% to about 2% by weight of the UV absorber may be incorporated. About 0.15% by weight is a preferred amount.

In accordance with a further aspect of the invention there is provided an article comprising a polymer or polymer composition in accordance with the invention.

According to an embodiment of this further aspect of the present invention, an intraocular lens (IOL) is provided which comprises a polymer comprising residues derived from methylmethacrylate having incorporated an UV absorbing amount of residues of UV absorber of formula (I) herein described wherein R is a  $-\text{CO.CR}^1$  =  $\text{CH}_2$  group and  $\text{R}^1$  is as defined hereinabove.

According to a further embodiment of the present invention, a contact lens is provided which comprises a polymer having residues derived from methylmethacrylate and UV absorbing amount of residues of UV absorber of formula (I) wherein R is a  $-\text{CO.CR}^1$  =  $\text{CH}_2$  group and  $\text{R}^1$  is as defined hereinabove.

Such intraocular or contact lens may comprise polymer material as herein described having from about 10 ppm to about 500 ppm of the UV absorber of formula (I) incorporated per part of polymer. From about 100 ppm to about 250 ppm is a preferred amount.

The intraocular lenses according to the present invention, may have haptics, eg two secured or affixed thereto or integral therewith and such haptics may have any of the known configurations or modifications thereof.

Both intraocular lenses (IOLs) and th contact lenses of the present inventi n may be produced by any of the conventional procedures and techniques per se known in the art. See, for example, US Patent No. 4102567; US Patent No. 4208364 ; US Patent N . 4158030 ; US Patent No. 3408429 ; US Patent N . 3361858 ; European Pat ent Applicati n No. 0328246 ; European Patent Applicati n No. 033348 ; Technical and Economic Effects of Contact Lens Production M thods by P. Cordrey, Optical W rid, 1972, Sept/Oct., pages 13 to 20 ; Intraocular Lens Implantation Design, E.S.P. F rd from Intraocular Lens Implantation edited by E.S. Rosen.

According to a further embodiment of th pres nt inv ntion, ey glasses ar produced having lens mad

of a polycarbonate material suitable for eyeglass lenses which has incorporated therein a UV absorbing amount of a compound of Formula (I). Aply the lens material will have from about 10 ppm to about 500 ppm of the UV absorber of Formula (I) per part of polycarbonate material. From about 100 ppm to about 250 ppm is a preferred amount.

5 For the IOLs, the contact lenses and the eyeglasses of the present invention the amount of the novel UV absorber which is incorporated can also be expressed as a weight percentage based on the weight of the polymer or polycarbonate material. Preferably, the weight percentage of the novel UV absorber incorporated is from about 0.1% to about 5% preferably from about 0.1% to about 2%. About 0.15% by weight is a preferred amount.

10 The invention will be illustrated by reference to the accompanying drawings in which :

Figure 1 shows an IR spectrum for BTAB.

Figure 2 shows a UV spectrum for BTAB.

The following examples are given to further illustrate the present invention.

15 Example 1

3,5-[Di(2H-benzotriazole-2-yl)] 2,4,4'-trihydroxy benzophenone (BTHB)

A solution of o-nitroaniline (11.1 g, 0.08 M) in concentrated hydrochloric acid (30 cc) was diluted with 30 cc of water and diazotised with a solution of sodium nitrite (5.69 g, 0.08 M) in water (20 cc) at 0°-5°C. The cold solution of o-nitrobenzene diazonium chloride was added over a period of one hour with stirring to a solution of 2,4,4' trihydroxybenzophene (9.2 g, 0.04 M), sodium hydroxide (7.29 g, 0.18 M), and sodium bicarbonate (22 g, 0.2 M) in water (300 ml) at 0°-5°C.

25 The red diazo compound was collected, washed to neutral with water, dissolved in 170 cc aqueous sodium hydroxide (13.6 g), and reductively cyclised with Zn dust (13.6 g) as room temperature in 24 hours.

Subsequently, the suspension was filtered, the residue washed with 10% aqueous NaOH ; the filtrate was combined with this extract and acidified with sulfuric acid while keeping the temperature below 10°C.

Precipitated crude ditriazole was collected by filtration, air-dried, extracted with ethanol to yield 9.25 g of product.

30 Example 2

Acryloyl chloride (2 g, 0.02 M) was added dropwise to a stirred solution of 3,5-[Di(2H-benzotriazole-2-yl)] 2,4,4'-trihydroxybenzophenone (4.6 g, 0.01 M) in 150 cc of 0.4 molar aqueous sodium hydroxide solution at 10°C. The reaction mixture was stirred at room temperature for 30 minutes and the precipitate collected by filtration.

The crude product was recrystallised from acetone-water.

Yield 2.8 g 90% pure by TLC

The product was

40 3,5-[Bis(2H-benzotriazole-2-yl)] 2,4,4'-dihydroxy, 4'-acryloyloxy-benzophenone (BTAB).

Example 3

45 Copolymerisation of the product of Example 1 with methylmethacrylate was carried out at 65°C in sealed tubes using USP-245 as an initiator.

This material has a polymerisation reactivity comparable to substituted styrenes, and hence can be incorporated into a wide variety of polymers by addition copolymerisation or grafting. Examples of polymers in which it can be incorporated are :

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By copolymerisation : polyolefins, polyacrylates, polymethacrylates, PVC, polystyrene and derivatised polystyrenes.

55 By grafting : polycarbonates, polyesters, polyacrylates and polymethacrylates.

Example 4

An intraocular lens was formed by first forming a UV absorber containing polymer and thereafter cutting out discs from the formed polymer sheet.

The polymer was found by mixing the following components:

Methylmethacrylate 99.7 part per hundred

5 BTAB 0.15 pph

OT100 (mould release agent)<sup>1</sup> 100 parts per million

USP245 (free radical initiator)<sup>2</sup> 0.15 pph

1 Sodium dioctyl sulphsuccinate [Cyanamicid]

2 2,2-Dimethyl-2,5-di(2-ethylhexanoyl peroxy) hexane.

10 After mixing the components were digassed by bubbling argon gas therethrough and then placing the mixture in a mould.

The mixture was then heated at 55°C for 10 hours after which the temperature was raised to 90°C for a further 24 hours.

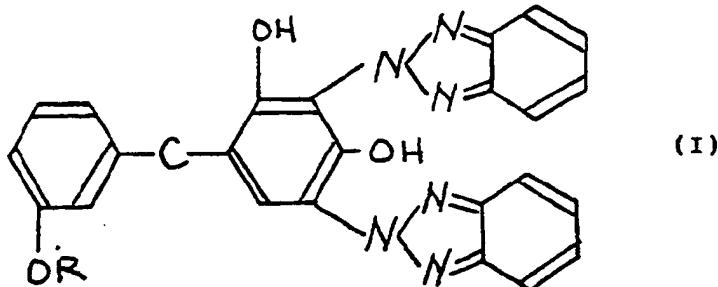
15 After polymerisation the formed sheet was post cured for 8 hours at 100°C and then cooled to room temperature.

Disc blanks were cut from the formed sheet and machined to produce intraocular lenses.

### Claims

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1. A compound of the formula (I):



25 wherein R is hydrogen or —CO.CR<sup>1</sup> = CH<sub>2</sub>, wherein R<sup>1</sup> is hydrogen or methyl.

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2. 3,5[Bis(2H-benzotriazol-2-yl)]2,4,4'-trihydroxy benzophenone.

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3. 3,5[Bis(2H-benzotriazol-2-yl)]2,4-dihydroxy4' -acryloyloxy benzophenone.

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4. A polymer composition comprising a UV absorbing amount of the compound of Formula I defined in claim 1.

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5. A polymer comprising residues derived from methyl methacrylate and residues derived from the compound defined in claim 1 wherein R is —CO.CR<sup>1</sup> = CH<sub>2</sub> and R<sup>1</sup> is as defined in claim 1.

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6. A polymer or polymer composition as claimed in claim 4 or claim 5 wherein the amount of compound of Formula (I) is from 0.1 to 5% by weight of the polymer or composition.

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7. An article produced from a polymer or polymer composition as claimed in any one of claims 4 to 6.

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8. An intraocular lens or a contact lens comprising a polymer as claimed in claim 5.

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9. An intraocular lens as claimed in claim 8 having at least one haptic attached thereto or formed integrally therewith.

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10. A lens according to claim 9 having two haptics.

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11. An article as claimed in claim 7 in the form of eyeglasses having lenses made from a polymer composition

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comprising a polycarbonate resin having incorporated therein a UV absorbing amount of the compound of Formula (I).

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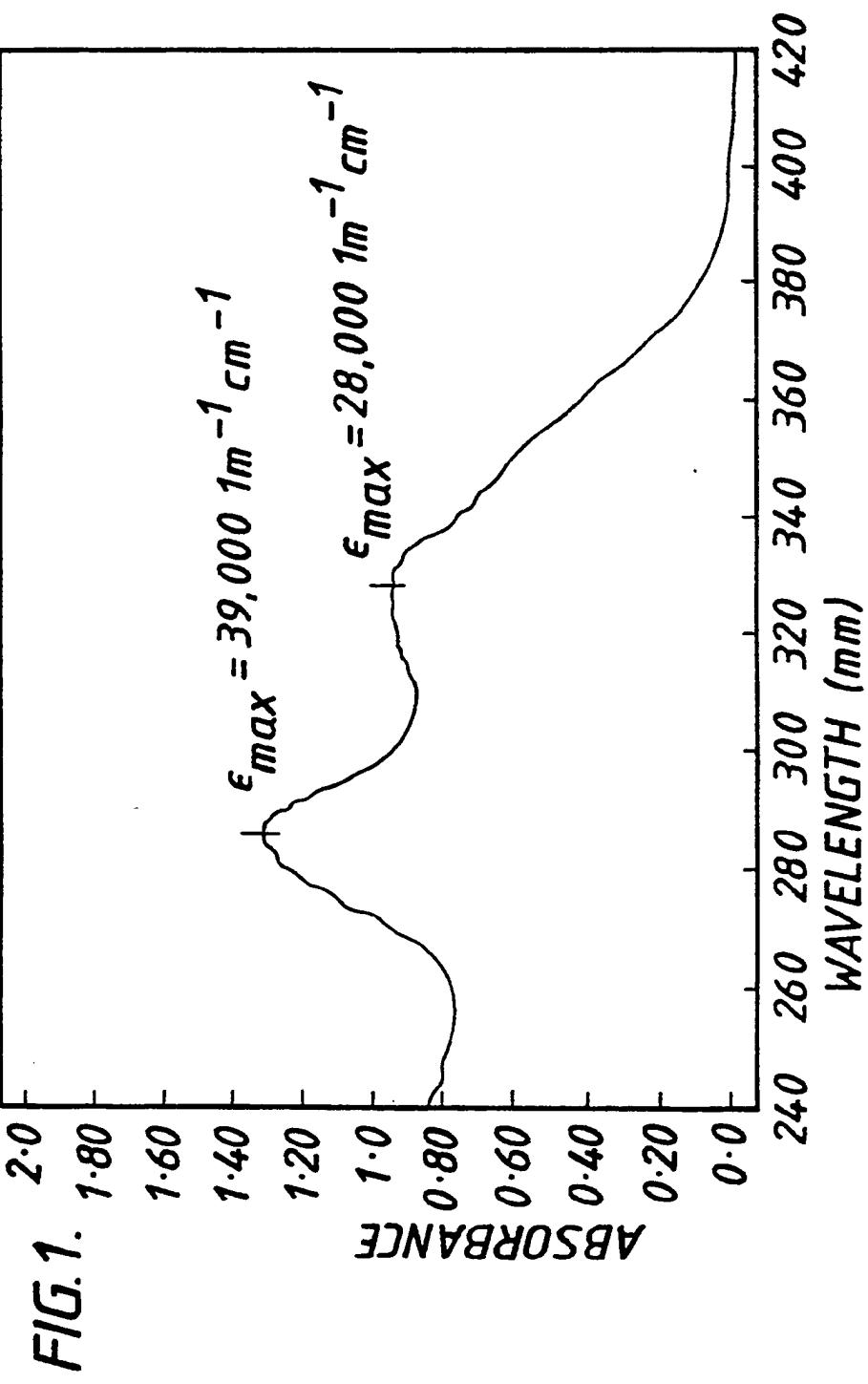
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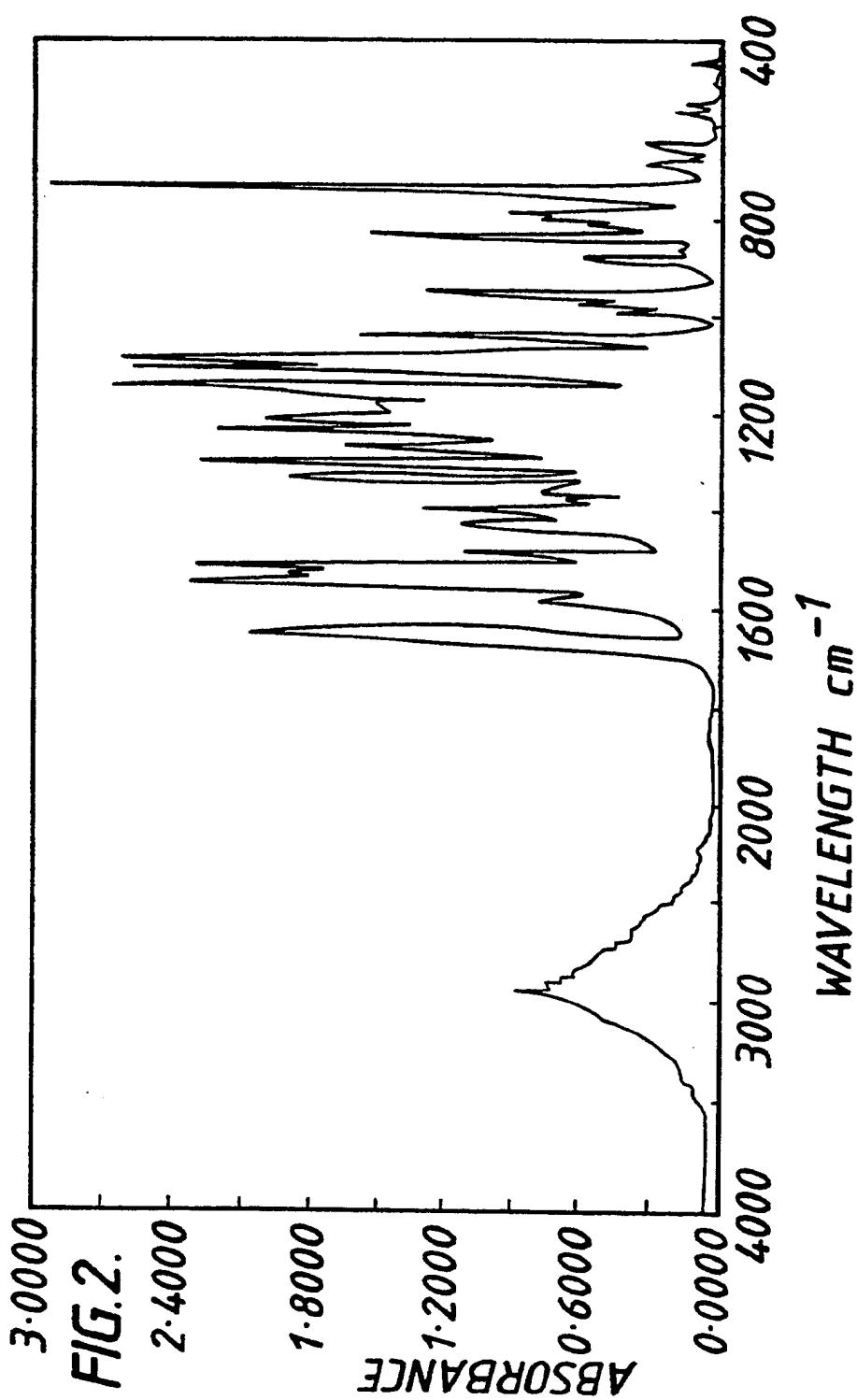
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(54) Bis(benzotriazoly)benzophenones and their use as UV absorbers.

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## EUROPEAN SEARCH REPORT

Application Number

EP 90 31 3102

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
Y	US-A-4 260 768 (D.H. LORENZ ET AL.) * the whole document * -----	1-11	C07D249/20 C08K5/3475 G02B1/04						
Y	US-A-4 716 234 (G.B. DUNKS ET AL.) * the whole document * -----	1-11							
Y	US-A-4 745 194 (O. VOGL ET AL.) * the whole document * -----	1-11							
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)						
			C07D						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>29 OCTOBER 1991</td> <td>ALLARD M.S.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	29 OCTOBER 1991	ALLARD M.S.
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THE HAGUE	29 OCTOBER 1991	ALLARD M.S.							
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